

THE STRUCTURAL PROPERTIES & FERROELECTRIC PROPERTIES OF SUCCINIC ACID DI-SODIUM SALT HEXA HYDRATE

CHANDRA KUMAR DIXIT¹ & A.K SRIVASTAVA²

¹Dept. of Physics, Feroze Gandhi Institute of Engineering & Technology, Raebareli, Uttar Pradesh, India

²Physical Research Laboratory Kamla Nehru Institute of Physical and Social Sciences, Sultanpur, Uttar Pradesh, India

ABSTRACT

The paper describes a simple and important ferroelectric nature of succinic Acid disodium salt hexa-hydrate. In this paper we have studied the variation of dielectric constant with temperature in compressed rectangular pellet form having silver paint electrodes using MOTWANE capacity, measuring unit DM-3750B. The plot shows a 2nd order phase transition at about 70°C and a sharp rise of dielectric constant at a very high value 9.4 at 149°C following a phase transition at this temperature.

The lattice structure described by the Bravis unit cell of the crystal growth governs the crystal symmetry. Though there are thousands of crystals in nature. The plot Vs electric field shows a hysteresis loop. This material shows ferroelectric behaviour which is used in many electronic s and optics applications.

KEYWORDS: Dielectric, Ferroelectric, Dielectric Loss, Pyro-Electric, Phase Transition, Hysteresis

INTRODUCTION

Ferroelectricity is phenomenon which was discovered in 1921. The name refers to certain magnetic analogies, though it is somewhat misleading as it has no connection with iron at all. Ferro-electricity has also been called Siegnette di-electricity material found to show ferroelectric properties such as a spontaneous polarization on cooled below the Curie point, ferroelectric domains and a ferroelectric hysteresis loop. A huge gap in the research on ferroelectric materials came in the 1950s, leading to the wide spread use of barium titanate based ceramics in capacitor applications and piezoelectric transducer devices.

All ferroelectric materials have a transition temperature called the Curie point(T_C), At a temperature $T > T_C$ the crystal does not exhibit ferro-electricity while for $T < T_C$ it is ferroelctric. On decreasing the temperature through the curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. If there are more than one ferroelectric phases, the temperature at which the crystal transforms from one ferroelectric phase to another is called the transition temperature. Early research work on ferroelectric transitions has been summarized by Nettleton (1922).

Pyro-electric crystals show a spontaneous polarization P_s in a certain temperature range. If the magnitude and direction of P_s can be reversed by external dielectric field, then such crystals are said to show ferroelectric behaviour, Hence, all single crystals and successfully poled ceramics which show ferroelectric behaviour are pyroelectric, but not vice versa. Ferroelectric crystals possess regions with uniform polarization called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a crystal separated by interfaces

called domain walls. The dielectric constant of a ferroelectric is, of course not a constant, but depends on the field strength at which it is measured; this is a consequence of the non-linear relationship between P and E. The dielectric constant is so defined is very high in the vicinity of the transition temperature, of the order of 10^4 - 10^5 . Above the transition temperature and obeys the Curie Weiss Law,

$$\epsilon = \frac{C}{T - \theta} + \epsilon_0$$

Where C' is constant, θ is characteristics temperature.

ϵ_0 is constant which occurs from electronic Polarization. In the vicinity of the transition temperature may neglect, since it is of the order of unity and. Likewise, the susceptibility.

$$\chi = \frac{C}{T - \theta}$$

EXPERIMENTAL DETAILS

The compound was procured from Fluka AG Switzerland. The compound sample was prepared by grinding mechanically into fine powder and it has been procured from Fluka Switzerland, about 99.9% paris form sample is avoiding from direct sun light and preferably the most of the sample preparation work has done at night.

The powder was heated upto 1073 K for 16hrs, then cooled to room temperature and grinded mechanically again for an hour to achieve fine powder the pellets were prepared with the compression machine (Flextural testing machine CAT No. AIM-313,S.No 91070 AIMIL. Associated, India) have pressure range 0-10 tonn wt/cm³. A suitable die was used having rectangular cross-section of the piston about 2.33cm² . The pellets so obtained were covered with the remaining powder and heated again at 1073 K for 16 hrs.

The pellet were polished to obtain smooth parallel surface and colloidal silver paint was used to form the electrodes the sample was annealed at 2/B of its melting point in a furnace for about 8-10 hrs. The capacitance of the sample was measured by the MOTWANE capacity measuring unit DM-3750B.

The dielectric constant and bulk ac conductivity (σ) of the sample were calculated by using following expressions –

$$\text{Dielectric constant(real)} \quad \epsilon = 1 + \frac{\Delta C}{C_0}$$

Where $\Delta C = C'' - C'$

C' is the capacitance of sample holder with specimen.

C'' is the capacitance of sample holder without specimen.

C_0 is the geometrical capacitance.

$$C_0 = \frac{0.68854A}{d} \quad (\text{in p. f})$$

Where A is the area of pellet, d is the thickness of pellet in cm.

Photo room temperature sample holder high temperature sample holder the loss tangent ($\tan \delta$) and parallel capacitance of the sample were directly measured as a function of temperature and frequency by the HP 4194 Impedance analyser.

The conductance $G = \omega C_p \tan \delta$

$$G = 2\pi f C_p \tan \delta$$

$$\text{a.c conductivity } \sigma_{ac} = \frac{GD}{A}$$

RESULTS AND DISCUSSIONS

The chemical formula of compound is $2\text{CH}_2\text{-COONa}_6\text{H}_2\text{O}$. This study shows temperature dependence electrical properties like (dielectric constant, dielectric loss) of compound. The temperature variation of dielectric constant of succinic acid disodium salt Hexahydrate is much interesting. The dielectric constant (ϵ) shows a 2nd order phase transition at about 70°C and thereafter a very sharp rise from almost very small to a very high value of dielectric constant (ϵ) 9.4×10^5 at 149°C Fig.1. There is a transition at this temperature also. The behaviour is similar to that observed in a complex of lead(smolenskil et.al²). The cooling curve (fig.2) follows the heat curve except the phase transition of 70°C .

The dielectric constant (ϵ) and dielectric loss at room temperature 15°C of the at 1 KHz. Frequency is 14.85 and 0.321 respectively. The values of $\tan \delta$ are found to increase with decrease in frequency. In the presence of electric field, the heat of dielectric loss is liberated. In a certain voltage, heat is liberated, the temperature of the dielectric then raises and the loss increases still more.

This dielectric loss ($\tan \delta$) is frequency dependent also and it has been attributed to a wide distribution of relaxation time due to barrier height. Seven crystal structures is also dependence upon point groups. The thirtytwo point groups can be further classified into crystals having a centre of symmetry crystals which do not possess a centre of symmetry. The crystals with a centre of symmetry include the 11 points groups labelled centro-symmetric in below table and these points groups do not show polarity.

Table 1

Crystal Structure	Point Groups	Centro Symmetric	Non Centro Symmetric
Triclinic	1,1	1	1
Monoclinic	2,m,2/m	2/m	2,m
Orthorhombic	222, mm2, mmm	mmm	222, mm2
Tetragonal	4,4,4/m,422,4mm,42m,	4/m (4/m)mm	4,4,422, 4mm,42m
Tri-gonal	-- 3,3,32, 3m,3m	-- 3,3m	-- 3,32,3m
Cubic	23,m3, 432, 43m,m3m	M3, m3m	23, 43m

The ferroelectric phase transitions are usually accompanied by pronounced anomalies near T_c in any other physical properties. Structural properties like unit cell dimensions. If D is electric displacements vector, ϵ is an alternating field and P is polarization vector and it is oscillatory, time dependent.

Hence-

$$\mathcal{E} = \mathcal{E}_0 e^{i\omega t}$$

$$P = P_0 e^{i\omega t - \delta}$$

$$D = D_0 e^{i\omega t - 2\delta}$$

Where δ being the phase angle.

The ratio of D and \mathcal{E} at static electric field is called dielectric permittivity, In the case of an alternating field this ratio becomes a complex quantity-

$$(\mathcal{E}' - \mathcal{E}'') = \frac{D_0}{\mathcal{E}_0} (\cos \delta - i \sin \delta)$$

By equating real and imaginary parts we get-

$$\mathcal{E}' = \frac{D_0}{\mathcal{E}_0} \cos \delta \quad \text{and} \quad K' = \frac{D_0}{\mathcal{E}_0 E_0} \cos \delta$$

$$\mathcal{E}'' = \frac{D_0}{\mathcal{E}_0} \sin \delta \quad \text{and} \quad K'' = \frac{D_0}{\mathcal{E}_0 E_0} \sin \delta$$

This indicate that the

$$\frac{\mathcal{E}''}{\mathcal{E}'} = \tan \delta \quad \text{and} \quad \frac{K''}{K'} = \tan \delta$$

$\tan \delta$ is known as dielectric loss or loss tangent. K'' is a quantity which is measure of the amount of energy absorbed by the system from applied dielectric field.

These ferroelectric is dependence upon temperature, frequency, polarization and diffraction of X-ray.

Table 2: Differences between Normal and Relax or Ferromagnetic

S. No.	Property	Normal Ferroelectric	Relax or Ferroelectric
1.	Dielectric temperature dependence	Sharp 1st or 2 nd order transition at Curie Point T_c	Broad diffused phase transition at Curie Point T_c
2.	Dielectric frequency dependence	Weak frequency dependence	Strong frequency dependence
3.	Dielectric behaviour in paraelectric range ($T > T_c$)	Follow Curie Wiess Law	Follow Curie Wiess Law
4.	Remnant Polarization (P_R)	Strong P_R	Weak P_R
5.	Scattering of light	Strong Anisotropy	Very weak Anisotropy
6.	Diffraction of X-rays	Line splitting due to deformation from para electric to ferroelectric phase.	No x-ray Line spectrum.

CONCLUSIONS

In this study compound has been synthesized and characterized through dielectric and ferroelectric behaviour, Its possible phase transition in heating cycle lies near at 149^0C and in cooling cycle Phase transition lies about 70^0C .

The dielectric parameter viz. ϵ and $\tan \delta$ are found to increase whereas the dielectric breakdown strength and the activation energy are found to decrease.

Hence variation of dielectric constant with temperature shows hysteresis succinic acid disodium salt Hexa-hydrate.

Table 3: Variation of Dielectric Loss Vs Temperature

Temperature (^0C)	$\tan \delta$ at 1KHz	$\tan \delta$ at 10KHz	$\tan \delta$ at 100KHz
34	0.321	0.217	0.173
35	0.371	0.216	0.172
38	0.392	0.241	0.186
39	0.421	0.327	0.193
40	0.472	0.330	0.197
42	0.492	0.330	0.198
45	0.498	0.345	0.203
48	0.499	0.353	0.205
49	0.532	0.421	0.350
50	0.589	0.445	0.373
52	0.632	0.468	0.398
54	0.667	0.567	0.492
57	0.693	0.568	0.501
59	0.762	0.613	0.583
60	0.891	0.721	0.693
65	0.931	0.728	0.718
70	0.998	0.759	0.731
75	1.113	1.01	0.921
80	1.732	1.11	1.07
82	1.786	1.516	1.213
83	1.832	1.526	1.218
89	1.935	1.720	1.326
90	1.962	1.826	1.416
95	1.997	1.828	1.532
96	2.137	1.932	1.637
98	2.261	2.013	1.782
100	2.432	2.127	1.936
101	2.486	2.131	1.998
102	2.516	2.212	1.999
103	2.553	2.234	2.103
110	2.594	2.3314	2.118
115	2.612	2.0132	2.001
119	2.673	2.1132	2.072
120	2.837	2.1721	2.113
122	2.932	2.3120	2.173
125	2.983	2.521	2.184
128	3.12	3.013	2.527
130	3.52	3.314	3.218
133	3.67	3.422	3.334
135	3.80	3.501	2.29

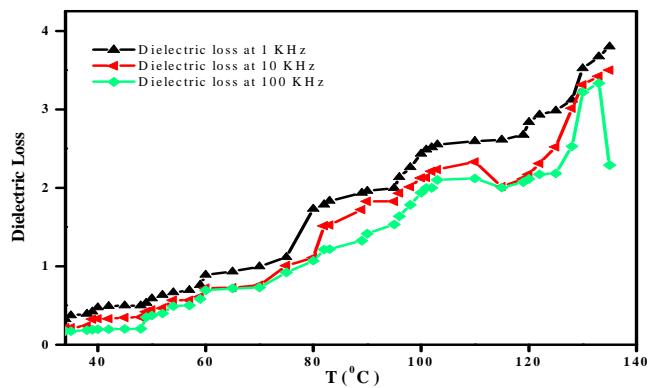
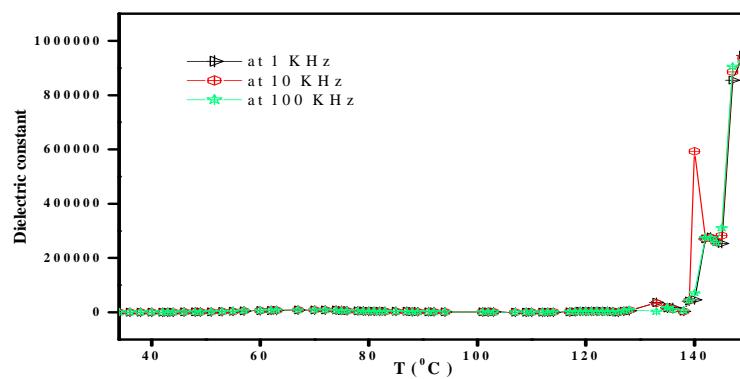


Table 4: Heating Cycle

Temperature (°C)	DIELECTRIC CONSTANT		
	at 1KHz	at 10KHz	at 100KHz
34	14.856	16.732	21.432
36	33.332	37.528	39.732
38	47.189	56.528	72.573
40	86.450	113.479	201.11
42	271.2	296.549	311.1
43	382.06	401.973	477.23
44	522.93	554.446	593.82
46	656.88	672.002	681.52
48	693.84	706.992	722.43
49	733.1	836.326	927.11
51	1001	1683.11	1997.92
53	2427.25	2629.74	2792.17
55	2890.14	3242.74	3997.99
57	4691.53	5324.12	5892.73
60	6123.4	6446.39	6617.74
62	6770.05	6813.59	7001.92
63	7139.56	7447.19	7855.74
67	8063.35	8317.49	8557.12
70	8640.72	8649.12	8656.92
72	8663.81	8456.52	8296
74	8132.63	7559.93	6911.82
75	6215.98	5910.78	5715.51
76	5522.93	5236.36	4978.05
78	4830.09	4613.78	4327.53
79	4137.25	4006.11	3947.52
80	3813.93	3729.42	3693.82
81	3629.17	3513.73	3472.12
82	3398.22	3304.51	2281.44
82	3213.47	3173.49	3096.71
85	3005.61	2975.31	2881.15
87	2728.48	2513.39	2497.27
88	2405.15	2324.16	2278.57
89	2151.11	1948.66	1837.15
91	1781.6	1658.27	1608.08
92	1527.55	1433.82	1396.12
94	1273.51	1212.48	1198.35
99	1148.80	1153.99	1154.59
101	1162.66	1097.53	994.1
102	936.33	891.159	842.157

Table 4 – Contd.,			
103	816.24	722.578	537.934
107	458.27	399.013	318.525
109	215.78	211.511	209.113
109	206.54	201.511	192.978
110	178.82	163.326	151.237
110	141.87	149.923	157.224
112	162.66	201.278	313.559
113	363.28	401.703	467.275
114	502.15	713.337	909.192
117	1167.28	1349.37	1444.92
118	1596.84	1953.18	2413.57
119	2751.57	2832.17	2899.23
120	2982.52	3135.43	3272.72
121	3444.41	3232.24	3153.24
122	2936.33	3030.21	3102.38
123	3167.28	3147.42	3131.62
124	3121.09	2936.46	2772.17
125	2636.1	2412.31	2001.14
126	344.418	553.623	817.573
127	3675.36	4337.44	4879.4
128	5291.99	7792.82	9002.12
133	36007.92	33021.74	3113.32
135	15453.65	16197.52	17094.27
135	17532.17	17632.09	17701.22
135	17763.12	17552.32	17453.44
136	17301.23	11083.65	9337.46
138	2751.57	3234.157	5541.27
139	41781.6	42791.82	43246.67
140	46400.53	592781.14	70967.22
142	270188.06	272622.52	274957.3
143	277116.47	275132.55	273609.3
144	260950.19	259234.34	257232.2
145	254021.78	282897.22	310715.5
147	854483.67	885723.43	905532.5
149	946862.43	936301.88	920791.5
150	909910.93	896053.73	822227.6
153	715915.55	693209.43	674422.6
154	623536.79	571765.61	521930.6
155	484968.66	527246.29	612726.9
156	854483.67	865345.51	887817.6



REFERENCES

1. W.P Mason, Phys. Rev. 73 854(1947).
2. J Valasek, Phys. Rev. 17, 475 (1921); 19,478 (1922); 20,644(1922); 24,560
3. B.T Mattias, Science, 113, 591 (1951); National Research Council, Wiley, New York, 1951.
4. B.C Frazar, M McKeown and R. Pepinsky, Phys. Rev 94, 1435 (1954).
5. G.Busch and P. Scherrer, Naturwiss, 23 737 (1935); G. Busch, Helv. Phys. Acta, 11 269(1938).
6. D.F. Rushman and M.A Strivens, Trans. Faraday Soc. 42A, 231 (1946).
7. E.T Jayenes, Ferroelectricity, Princeton Univ. Press Princeton, 1953 chaps. 1,3.
8. C.J.F Bottcher; Theory of electric Polarization, Elsevier, New York, 1952 pp63.
9. L. Onsager, J.Am. Chem. Soc. 58, 1486 (1936).
10. G.H. Jonker and J.H Van Santen, Science, 109,632 (1949).
11. W.P Mason; Peizo electric crystals and their applications Van Nostran New York (1950).
12. A.F Devonshire, Phil. Mag. 40.1040 (1949).
13. W.G Cady, Peizoelectricity, McGraw Hill, New York 1946.
14. A.F Devoshire; Theory of Ferro electrics Phil. Mes. Vol.3 April (1954) pp.85.
15. G. Shirane, F.Jona and R. Pepinsky "Some Aspects of Ferro electricity" Proc. IRE, Dec. (1995) pp.1738.
16. J.H Van Saten and W. Oechow Ski. Physical 14,545 (1948).
17. H.T Evans; ActaCryst. 4, 377 (1951).
18. Kumar. A; Prasad A, Choudhary, S.N and Choudhary, R.N.P (2004); Mat. Lett.
19. Gupta R.N and Mishra, M (1981); Ind. J. Pure and App. Phys. Vol. 17 pp. 1151-53.
20. Scaif. B. K.P (1989); Principle of Dielectric (Clareden Press).
21. A.J Dekker; Solid state Phys. United Kingdom (1958) pp.190 and 191.